



## Organic components in hair-ice

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Hair-ice is a rather unknown phenomenon. In contrast to generally known frost needles, originating from atmospheric water and expanding e.g. from plant surfaces in all directions, hair ice grows from the basis of wet, rotten hardwood. The hair-like, flexible, linear structures may reach up to 10 cm in length without any ramifications. Hair-ice appears to be related to the biological activity of a fungus mycelium within the wood.

Hair-ice can attract winter-active Collembolus (snow flea, *Isotoma nivalis*). At the onset of hair-ice melt a very thin fibre becomes apparent, which carries brownish pearl-like water drops. Therefore, it is supposed that organic substances are inherent, which could possibly act as freezing catalyst as well as recrystallization inhibitor. The aim of this work was the chemical characterization of organic substances contained in hair-ice.

First analyses of melted hair-ice show a total organic carbon (TOC) value of 235 mg/l in contrast to 11 mg/l total nitrogen. Most of inherent nitrogen (70 %) exists thereby as ammonium. Screened by different (mass spectrometric) methods, no evidence could be found for the initially expected organic substances like proteins, lipids, small volatile substances or carboxylic acids.

By coupling of Ultra Performance Liquid Chromatography with a triple quadrupole mass spectrometer (UPLC-MS) a non-resolved chromatogram from a melted hair-ice sample was received. Averaged spectra from different regions are similar among themselves with a broad peak spreading over the mass range 100-650 Da with favored intense, odd-numbered peaks. Such spectra are similar to dissolved organic matter (DOM), known e.g. from terrestrial and marine waters, soil extracts or aerosols. In the next step, samples were desalted and concentrated by solid phase extraction (SPE) and subsequently analyzed by flow injection analysis (FIA) in a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FTICR-MS), equipped with an ESI source and a 7 T supra-conducting magnet (LTQ-FT Ultra, ThermoFisher Scientific). This technique is the key technique for the analysis of complex samples due to its outstanding mass resolution (used 400.000 at  $m/z$  400 Da) and mass accuracy ( $\leq 1$  ppm), simultaneously providing molecular level details of thousands of compounds. The characteristics of the FTICR-MS hair-ice spectra with as many as ten or more peaks at each nominal mass are discussed together with highly resolved spectra from water and soil samples different sources, respectively.

Complete manual formula assignment for structure elucidation would be extremely time consuming, therefore, we used an automated post processing based on SciLab for exploitation of the data with the aim of an unambiguous assignment of as many peaks as possible. Once the formulae had been assigned, the obtained mass lists were first checked randomly and afterwards transformed into Excel format for further post-processing and description.

Most important is the van Krevelen diagram, usually two-dimensional as atomic ratio H/C versus atomic ratio O/C, widely used to classify samples regarding polarity and aromaticity. By comparison with two references (Hockaday 2007, Sleighter 2007), which arranged various biopolymer substance classes in such Van Krevelen plots, lignin could be detected as the main hair-ice component.